PATENT COOPERATION TREATY

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PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
4519/WO/97+		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/IL99/00045	25/01/1999	26/01/1998
International Patent Classification (IPC) or national classification and IPC C22B7/00		
Applicant ROSENBERG, Ariel		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 7 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 13 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☒ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
19/08/1999	03.05.2000
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Boureau, J-L Telephone No. +49 89 2399 8454

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/IL99/00045

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-3,5-28	as originally filed			
4,4a-4b	as received on	03/04/2000	with letter of	29/03/2000

Claims, No.:

1-41	as received on	03/04/2000	with letter of	29/03/2000

Drawings, sheets:

1/1	as originally filed

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-21,23-39
	No:	Claims	22,40,41
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-21,23-39
Industrial applicability (IA)	Yes:	Claims	1-41
	No:	Claims	

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

1. Section V - Novelty, inventive step

Reference is made to the following documents:

D1: WO 97 29214 A (RESCH HERIBERT ;EDLINGER ALFRED (CH); HOLDERBANK FINANC GLARUS (CH) 14 August 1997

D2: US-A-4 317 800 (SLOTERDIJK WIJTZE ET AL) 2 March 1982

D3: WO 95 33686 A (TNO ;LUGGENHORST HENDRIK JAN (NL); PEEK EDGAR MANFRED LAWRENCE (NL) 14 December 1995

D4: WO 95 22373 A (COMMISSARIAT ENERGIE ATOMIQUE ;CARRE DOMINIQUE (FR); TEMPLIER JEAN) 24 August 1995

D5: VDI Berichte 1033, Techniken der Restmüllbehandlung, Dipl.-Ing. H.-U-Hartenstein and Dr.-Ing. W. Schumacher, "Anforderungen an die Anlagetechnik einer modernen Müllverbrennungsanlage sowie deren Umsetzung", Conference held in Würzburg, 20-21 April 1993, VDI Verlag GmbH, Düsseldorf (Germany), pp. 165, 170-173.

D6: Chemical Dictionary, Grant & Hackh's, 5th edition, 1987, Mc Graw-Hill Book Company, New-York (USA), pp. 130, 131

The documents D5 and D6 were not cited in the international search report. Copies of the documents are appended hereto.

1.1 Claim 1

1.11 Citation D1 discloses a process for treating wastes in which the incinerated or pyrolysed wastes are halogenated and halides of copper and of heavy metals like Pb, Zn are extracted. Citation D1 discloses steps a) and c) of claim 1 of the present application, as explained below.

The specification of the present application makes clear that the primary heat treatment of the invention under a controlled amount of oxygen may be carried out either in the presence or in the absence of oxygen (see especially the examples), i.e. it may be either an oxidation or a pyrolysis step. Since the wastes treated in accordance with D1 have been either incinerated or pyrolysed, step a) of claim 1 of the present application is regarded as part of the process known from document D1. In particular pyrolysis is a treatment which is substantially conducted in the absence of oxygen, i.e. the amount of oxygen in the reactor is substantially reduced in a controlled manner. As illustrated by document D5, pages 171 and 172, wastes were processed prior to the priority date of the present application in modern incinerators under controlled amounts of oxygen.

Claimed step (c) is known from D1, page 1, lines 34, 35.

Concerning step (b) of claim 1, document D1 necessarily involves halogenation of the incinerated or pyrolysed residues because metal chlorides mentioned in D1, page 1, lines 34, 35 obviously result from the transformation of metal compounds in chlorides. In this regard, the term "halogenation" just means that halogen is introduced into a compound; it may be carried out with halogen or halogenides either in the gas phase or the liquid phase. Halogenation with gaseous halogen is only a specific kind of halogenation. For instance, the term "chloridization" is used for chlorinating metal ores with chlorine (see D6).

Although the formulation of step (b) of claim 1 does not exclude halogenation by treatment with chlorine or bromine formed in-situ and although such in-situ halogen formation is likely to take place in the process of D1, e.g. by heating chlorine-containing organic solvents at 650°C (page 1, lines 30-33), halogenation by chlorine or bromine is not regarded as disclosed by document D1.

Consequently, the process of claim 1 only differs from the process known from document D1 by the following feature:

- halogenation is carried out by treatment with chlorine, bromine or a mixture thereof, in the presence of a halogenation catalyst.

Although the process of claim 1 may be regarded as novel, it does not involve an inventive step to form metal chlorides by halogenation with gaseous halogens. This is an alternative route which is known in the same technical field, e.g. from document D2, column 6, lines 8-24. According to this passage of D2, roasting of metal scrap (as disclosed in DE-B-2 316 318) involves halogenation of metals with halogen gas. Such reductive roasting is used in document D1 (see page 1, line 35 to page 2, line 3).

Moreover, catalysing a chemical reaction in order to improve the efficiency of the reaction belongs to the basic knowledge of a chemist.

Therefore, the process of claim 1 does not involve an inventive step (Article 33(3) PCT).

One comes to the same conclusion by replacing document D1 by document D4 (page 1, lines 4-7; page 3, line 12 to page 6, line 5).

1.2 Claims 2-21

The features of the sub-claims 2-17, 20, 21 are known from the above cited prior art.

Claims 18 and 19 relate to embodiments which appear to lie within the common knowledge of the one skilled in the art. Thus, they do not seem to involve an inventive step (Article 33(3) PCT).

1.3 Claim 22

1.31 The apparatus according to claim 22 is not novel in view of Figure 2 of document D2. In this Figure, the separation units (5, 8, 11) are connected to the halogenation chamber which comprises an inlet and a outlet. An apparatus does not become novel merely because other materials are circulated through some parts of the apparatus.

Therefore, claim 22 does not meet the requirements of novelty (Article 33(2)

PCT).

1.4 Claims 23-41

The features of the sub-claims 23 to 41 are either known or rendered obvious by the cited prior art.

2. Section VII - Certain defects

Independent claim 1 is not in the two-part form in accordance with Rule 6.3(b) PCT, which in the present case would be appropriate, with those features known in combination from document D1 (see paragraph 1.11 above) being placed in the preamble (Rule 6.3(b)(i) PCT) and with the remaining features being included in the characterising part (Rule 6.3(b)(ii) PCT).

be easily decompounded to form SiO_2 and HCl from which the Cl is recycled.

WO 97/29214 discloses a process for the separation of metals from incinerated garbage residue and slag, the residue and slag from garbage incinerational pyrolysis being heated at over 650°C under reducing conditions together with substances containing chlorines or chlorides, such as flue gas cleaning residues, $CaCl_2$ from the production, cooking salt, organic solvents or electroplated sludge containing chlorine, whereupon copper chlorides and volatile heavy metal chlorides are drawn off in the gas phase.

USP 4,317,800 discloses a process for reducing environmental pollution resulting from disposal of waste-containing halogenated hydrocarbons by some simultaneous treatment with used metal and/or metal scrap at elevated temperatures. The halogenated hydrocarbons are pyrolized, and the resulting hydrogen halide-containing gas is brought into contact with the metal at elevated temperatures so as to form halogenites that are volatile under the conditions supplied.

WO 95/33686 discloses a method for extracting metals from metal-containing materials, especially waste, by pyrohydrolysis. The metal-containing materials are made to react at 700-1100°C, with a gas

composition comprising 25-45% water vapor, 0.1% carbon dioxide, 2-20% hydrogen chloride and 0-15% carbon monoxide, the remainder being nitrogen and possibly oxygen, and the metals are extracted in the form of volatile metal chlorides.

WO 95/22373 discloses a method for removing pollutants consisting of heavy metals and toxic elements from fly ash and few purification residues resulting from waste incineration. The waste is subjected to chlorination, thermal treatment, sulfuration for the twofold purpose of the removal and concentration of a fraction containing heavy metals and toxic elements.

Most wastes contain more than one element and several unknown contaminates. Most wastes contain both organic and non-organic elements.

The organic waste materials are in most cases a mixture of various chains of molecules together with various elements incorporated, as well as other non-organic materials, and are usually difficult in recycling, and they create environmental problems.

Chlorination of organic material can produce hazardous, toxic and cancerous elements.

It is a purpose of the present invention to provide a process for destruction of hazardous and/or toxic industrial waste in which the toxic and/or the hazardous compound waste is reduced into less toxic, or non toxic material, and/or less hazardous or non hazardous material, and the size and quantity of said waste is also reduced.

NEW CLAIMS

1) A highly efficient recovery process for the treatment of multi-element wastes which comprises the steps of:

a) a primary heat treatment of the waste in the presence of a controlled amount of oxygen;

b) after the completion of said heat treatment, halogenation of the product of said heat treatment by treatment with chlorine, bromine or a mixture thereof, in the presence of a halogenation catalyst; and

c) separation of the metal halide products of said halogenation.

2) A process according to claim 1 in which said multi-element waste is unsorted.

3) A process according to claim 1 in which the waste to be recovered is such that has been mechanically prepared in a process which includes any one or more of the steps of shredding, crushing, milling and briquetting.

4) A process according to claim 1 in which said primary heat treatment further comprises mechanically agitating the waste during said treatment.

5) A process according to claim 1 in which the primary heat treatment is carried out in such a way that any one or more of the actions selected from the group which consists of evaporation of water and/or organic material, carbonization, destruction and/or cracking of organic material, and reduction of metal oxides to metals and/or metal carbides, are achieved.

6) A process according to claim 1 in which the primary heat treatment is carried out under atmospheric pressure or higher pressure, optionally in the presence of gases, preferably hydrogen, capable of cracking the organic or inorganic material.

7) A process according to claim 1 in which at least a portion of the heat energy afforded in the primary heat treatment is used in the halogenation reaction.

8) A process according to claim 1 in which at least a portion of the product of the primary heat treatment is used as a catalyst in the halogenation reaction.

9) A process according to claim 8 in which said products to be used as catalysts are selected from the group which consists of carbon, bromine, carbon, CO, CO_2 and SO_x and NO_x compounds.

10) A process according to claim 1 wherein the primary heat treatment is performed in an oven.

11) A process according to claim 10 wherein said oven is at a temperature of less than about 1000°C.

12) A process according to claim 1 wherein the primary heat treatment is performed in a metallic molten bath.

13) A process according to claim 12 wherein said molten bath is at a temperature of between 500°C and 1600°C.

14) A process according to claim 1 which further comprises a secondary heat treatment comprising heating the gaseous flow which results from the primary heat treatment to a temperature of more than 1200°C.

15) A process according to claim 1 in which said halogenation step further comprises mechanically agitating the waste during said step.

16) A process according to claim 1 in which the halogenation reaction is performed at a temperature of between ambient temperature and 1500°C.

17) A process according to claim 1 in which the halogenation reaction is performed at a temperature of between 300°C and 1500°C, and preferably between 700°C and 750°C.

18) A process according to claim 1 in which the waste comprises a substantial percentage of any of the metals selected from the group which consists of Ag, Pt and Pd, and the halogenation reaction is performed by using a mixture of bromine and chlorine.

19) A process according to claim 18 in which said mixture of chlorine and bromine comprises between 93% and 99% chlorine and the remainder is bromine.

20) A process according to claim 1 in which at least a portion of the excess halogen gas remaining from the halogenation reaction is recycled back to the halogenation chamber.

21) A process according to claim 1 in which the separation of the metal halides is by means of any one or more of the group selected of gaseous or liquid fractional deposition, distillation, fractional distillation, filtration,

selective chemical vapor deposition, settling, selective oxidation, selective halogenation, selective evaporation, selective dissolution and selective extraction.

22) An apparatus for a high efficient recovery process for the treatment of multi-element wastes, which comprises:

I) a primary heat treatment chamber (3);

II) a halogenation chamber (9); and

III) a separation unit (11 to 15) connected to said halogenation chamber;

IV) said primary heat treatment chamber comprising a waste inlet (2), a flue-gas outlet (20) and means of heating; and

V) said halogenation chamber comprising a means of heating, a halogen compound inlet (10) and an outlet (16).

23) An apparatus according to claim 22 in which the flue-gas outlet of said primary heat treatment chamber is connected to said halogenation chamber by means of a conduit, which comprises a valve.

24) An apparatus according to claim 22 in which said separation system comprises one or more of the units selected from the group which consists of fractional deposition unit, distiller, filter, settler, selective chemical

vapor deposition unit, selective oxidation chamber, selective halogenation chamber, evaporation chamber and selective dissolution unit or any combination thereof.

25) A apparatus according to claim 24, wherein the separation system comprises fractional deposition unit or selective chemical vapor deposition unit.

26) An apparatus according to claim 22 in which said separation system is a gaseous fractional deposition system; the inlet of which is connected to the outlet of said halogenator, by means of a conduit.

27) An apparatus according to claim 26 in which the outlet pipe comprised in the fractional deposition system is connected directly to the halogenation chamber, and said pipe comprises a one-way valve in the direction from the fractional deposition system to the halogenation chamber.

28) An apparatus according to claim 22 which further comprises an secondary combustion chamber (5) and a heat exchanger (8); said secondary combustion chamber comprising a means of heating, a gas

inlet, an air inlet, and a flue gas outlet; said gas inlet of said secondary combustion chamber being connected by means of a conduit to the flue gas outlet of said primary heat chamber; said heat exchanger comprising an inlet and an outlet; the flue gas outlet of said secondary combustion chamber being connected by means of a conduit to the inlet of said heat exchanger.

29) An apparatus according to claim 28 which further comprises a scrubber, a filter, a blower and a stack; said scrubber comprising an inlet and an outlet; the outlet of said heat exchanger being connected, by means of a conduit to the inlet of said scrubber; said filter comprising an inlet and an outlet; the outlet of said scrubber being connected, by means of a conduit to the inlet of said filter; said blower comprising an inlet and an outlet; the outlet of said filter being connected, by means of a conduit to the inlet of said blower; said stack comprising an inlet and an outlet; the outlet of said blower being connected, by means of a conduit to the inlet of said stack.

30) An apparatus according to claim 29, wherein the scrubber and the filter are connected to the halogenation chamber by means of conduits, to

recycle material recovered and collected by said scrubber and filter to said halogenation chamber.

31) An apparatus according to claim 29 in which said filter is selected from the group which consists of fabric filter, electrostatic filter, and high temperature filter.

32) An apparatus according to claim 24 which further comprises any one or more of the units selected from the group which consists of shredder, crusher, mill, briquetter doser, and sludge feeder, which are connected to the primary heat treatment chamber; providing that the outlet of the unit connected to the primary heat treatment chamber is connected to the inlet of said primary heat treatment chamber by means of a conduit; further providing that in the event that said apparatus comprises two or more of the above units, said units are connected succeedingly, in any combination and/or order, and are connected so by means of conduits.

33) An apparatus according to claim 22 which further comprises any one or more of the units selected from the group which consists of shredder, crusher, mill, briquetter, doser and sludge feeder which are connected between the primary heat treatment chamber and the halogenation chamber; providing that the outlet of the unit which is connected to the

halogenation chamber is connected to the inlet of said halogenation chamber by means of a conduit; further providing that the outlet of the primary heat treatment chamber is connected to the inlet of the unit which is connected to said primary heat treatment chamber by means of a conduit; further providing that in the event that said apparatus comprises two or more of the above units, said units are connected succeedingly, in any combination and/or order, and are connected so by means of conduits.

34) An apparatus according to claim 22 in which said primary heat treatment chamber further comprises a means of agitating material.

35) An apparatus according to claim 34 in which said means of agitating is a means selected from the group which consists of fixed fluidized bed vibrating grid, walking grid and rotary kiln.

36) An apparatus according to claim 22, wherein the primary heat treatment chamber comprises a pressurized vessel.

37) An apparatus according to claim 22 in which said halogenation chamber further comprises a means of agitating material.

38) An apparatus according to claim 37, in which said means of agitating is a means selected from the group which consists of fixed fluidized bed vibrating grid, walking grid and rotary kiln.

39) An apparatus according to claim 22, wherein the halogenation chamber comprises a pressurized vessel.

40) An apparatus according to claim 22, in which the primary heat treatment chamber is placed horizontally, vertically or at any other advantageous angle.

41) An apparatus according to claim 22 in which the halogenation chamber is placed horizontally, vertically or at any other advantageous angle.